

FLUIDS RELATED TO TUNGSTEN ORE DEPOSITS IN NORTHERN PORTUGAL AND SPANISH CENTRAL SYSTEM: A COMPARATIVE STUDY

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Abstract: A comparative study of P-T-X fluid evolution in several Iberian tungsten deposits has been carried out using microthermometric and Raman data on representative deposits of Northern Portugal (Panasqueira and Borralha) and Spanish Central System (San Rafael, Cabeza Mediana, Cabeza Lijar). Three main types of fluids have been distinguished: (i) magmatic hypersaline aqueous fluids (only present in Spanish Central System); (ii) "metamorphic" aqueous-carbonic fluids (H₂O-NaCl-CO₂-CH₄); and (iii) aqueous fluids (H₂O-NaCl). The fluid evolution is characterized by dilution of aqueous-carbonic fluids, accompanied by a decrease of the volatile phase density and cooling. The W-mineralisation is always related to aqueous-carbonic fluids, resulting from the interaction between water and C-bearing metamorphic host rocks. The Hercynian granites of Iberia are thus considered to have played a role on ore forming processes rather distinct than that previously thought, as no typical magmatic signature is found except in the earliest stages responsible for the greisen formation in the Spanish Central System. The main role of the granites appears to be a heat supply at the origin of fluid convection, rather than a fluid or a metal source.

Key words: tungsten, fluid inclusions, Northern Portugal, Spanish Central System.

Resumen: En este trabajo se ha realizado un estudio comparativo de las condiciones P-T-X de los paleofluidos asociados a diferentes mineralizaciones de wolframio de la Península Ibérica. Para ello se ha realizado un estudio microtermométrico y espectroscopia Raman, con recopilación también de datos previos de inclusiones fluidas en algunas mineralizaciones representativas de wolframita con sulfuros del Norte de Portugal (Panasqueira, Borralha) y del Sistema Central Español (San Rafael, Cabeza Mediana, Cabeza Lijar). Se han distinguido tres tipos fundamentales de fluidos: (i) fluidos hipersalinos de origen magmático (solamente en las mineralizaciones del Sistema Central); (ii) fluidos acuoso-carbónicos (H₂O-NaCl-CO₂-CH₄) que se pueden interpretar como de "tipo metamórfico"; y (iii) fluidos (H₂O-NaCl). La evolución de estos fluidos está caracterizada por una dilución del fluido acuoso-carbónico, una disminución de la densidad de la fase volátil con el descenso de temperatura. La deposición del wolframio está siempre relacionada con la presencia de fluidos acuoso-carbónicos, resultado de la interacción de agua con rocas metamórficas carbonáceas. No se han encontrado evidencias de participación de fluidos magmáticos, excepto aquellos fluidos hipersalinos relacionados con greisenizaciones tempranas en granitos del Sistema Central Español.

Palabras clave: wolframio, inclusiones fluidas, Norte de Portugal, Sistema Central Español.

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The Iberian Peninsula displays numerous similar W deposits located in Central Iberian Zone (CIZ) and Galicia-Trás-os-Montes Zone (GTMZ). They are spatially related with post-tectonic biotite-granites. All the studied examples from the Iberian Peninsula display rather similar fluid evolution with the Hercynian W deposits. In order to compare the P-T-X fluid evolution in these deposits, a study has been carried out on the most important Portuguese ore deposits: Panasqueira and Borralha deposits in Northern Portugal and on W-occurrences, San Rafael, Cabeza Mediana, Cabeza Lijar in the Spanish Central System (Table I). The studied samples were selected based upon their

different geological settings, and assumed from similar age (300 to 280 Ma, Caballero *et al.*, 1992 for SCS; Pinto *et al.*, 1987 for Northern Portugal), as fluid circulation occurs in the upper crust during the late Carboniferous uplift of the Variscan belt. The fluid evolution reconstruction is based on previous and new microthermometric and Raman studies of fluid inclusions.

Geological setting

The studied W-deposits are located in Central-Iberian (CIZ) and in Galicia-Trás-os-Montes Zones

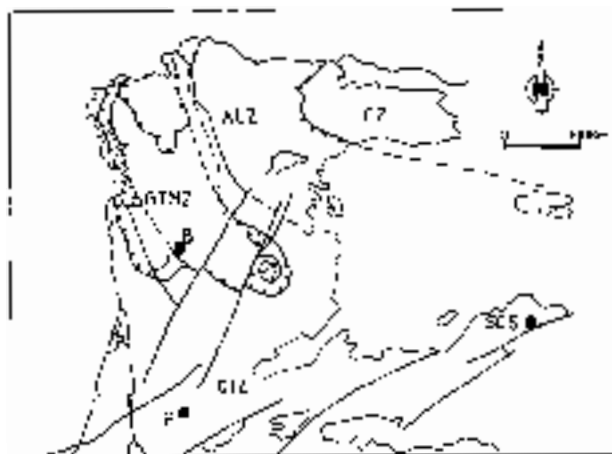


Figure 1.- Geotectonic zones of the Iberian Peninsula (CZ- Cantabrian zone; ALZ- Asturian-Leonese zone; GTMZ- Galicia-Trás-os-Montes Zone; CIZ- Central Iberian Zone) and studied tungsten deposits (P- Panasqueira; B- Borralha; SCS- Spanish Central System).

(GTMZ) (Fig. 1). The CIZ constitutes the most important zone of the Hesperic Massif. It is characterised by the presence of autochthonous metamorphic formations, Cambrian and late Precambrian in age. The GTMZ is characterised by Precambrian allochthonous massifs, predominantly mafic and ultramafic, surrounded by parautochthonous metasedimentary sequences mostly from Ordovician-Silurian including an important volcano-sedimentary complex and organic rich terms.

The two zones are also characterised by an important plutonic magmatism represented by Hercynian synorogenic granites. Based upon their petrographic, geochemical and geologic characteristics, these granites can be schematically divided into two main groups: the two mica granites and the biotite granites. The two mica granites can be considered syn-metamorphic peak, syn-collisional and approximately syntectonic. The biotite-granites are late and post-tectonic, and their intrusion is linked to distensive late stages. (Ferreira *et al.*, 1987; Villaseca *et al.*, 1993). The studied W(Sn) quartz vein deposits are spatially related to post-metamorphic, post-tectonic biotite-granite stage.

Mineralogy

The mineral assemblages reveal two main mineralising stages separated in time by fracturing episodes and consist of successive crystallisation of - (Sn) W oxides (oxide silicate stage, (OSS)) and Mo-As-Cu-Zn-(Pb) sulphides (main sulphide stage, (MSS)) (Noronha, 1974, 1984, 1990; Thadeu, 1977; Kelly and Rye, 1979; Vindel, 1980; Bussink 1984; Mangas, 1987; Polya, 1989; Noronha *et al.*, 1995).

The dominant component of the veins is quartz. Four morphological and textural types of quartz can be distinguished: (1) milky quartz (QI) with a slight deformation and containing abundant fluid inclusions; (2) quartz (QII) with a mosaic texture and few fluid inclusions; (3) clear quartz (QIII) crystals; (4) later

clear euhedral quartz showing vuggy textures (QIV). QIII and QIV have been only observed in the portuguese samples.

The main ore stage "oxide silicate stage": cassiterite, when present, is one of first minerals and is, generally, contemporaneous of quartz, muscovite and topaz (\pm arsenopyrite) that represent the earliest mineral association; wolframite is always the main oxide. However, at Borralha the absence of cassiterite and the presence of scheelite is noticed for the "oxide silicate stage". Muscovite, quartz and topaz represent the earliest mineral association at Panasqueira. The early quartz deposition (QI) is preceded by a strong K-mica alteration of the granitic wall-rock in the SCS. Economically this first stage is by far the most important because wolframite and scheelite are present.

The "main sulphide stage" is essentially characterised by the association of QII with sulphides: arsenopyrite, pyrite, pyrrhotite, sphalerite, chalcopyrite and stannite, at Panasqueira for instance (Kelly and Rye, 1979). At Borralha, this stage is characterized by the absence of arsenopyrite and the presence of molybdenite and bismuthinite (Noronha 1984). In the SCS, saccharoidal quartz (QII) is associated with the crystallisation of pyrite, chalcopyrite, sphalerite, sometimes galena, chlorite and minors amounts of scheelite (Vindel *et al.*, 1995).

Pyrite, marcasite, galena, Pb-Bi-Ag sulphosalts, quartz (QIII) and siderite characterize a latter stage, the "pyrrhotite alteration stage" (Kelly and Rye, 1979; Noronha, 1990).

During a later stage, dolomite and calcite are observed at Panasqueira (Kelly and Rye, 1979) while at Borralha a chlorite-adularia-quartz (QIV) association is found (Noronha, 1984).

Fluid inclusion studies

Analytical methods

Microthermometric characterisation of the fluid inclusions was performed on wafers (300 μ m thick) using a heating-freezing Chaixmeca stage (Poty *et al.*, 1976) and a Linkam THMSG 600 (Shepherd, 1981). The stages were calibrated with melting-point of solid standards at $T > 25$ °C on natural and synthetic inclusions at $T < 0$ °C. The rate of heating was monitored in order to get an accuracy of ± 0.2 °C during freezing, and ± 1 °C when heating over the 25 °C -400 °C range and ± 4 °C over the 400 °C -600 °C range.

Salinity, expressed as equivalent weight % of NaCl and fluid density of volatile-free fluid inclusions in quartz, were determined by microthermometry (Potter, 1977; Potter *et al.*, 1978). In volatile-bearing fluid inclusions, CO₂ was identified by melting of a solid below -56.6 °C. The volumetric fraction of the aqueous liquid (flw) have been estimated at room temperature by reference to the volumetric chart of Roedder (1972). Molar fractions of CO₂, CH₄, H₂S and N₂ were determined in individual inclusions by micro-Raman

	Q-W veins	Wall rock	Hydrothermal alteration	Age	Ore Assemblage	References
Spanish Central System	San Rafael C. Mediana Cabeza Lijar	Peraluminous leucogranites	Greisenization Chloritization	300-290 m.y.	QI-W-Sn QII-Fe-Cu-Zn- Pb sulphides	Garcia (1997) Vindel et al. (1995) Quílez (1994) Martin (1995) Caballero et al. (1992)
Northern Portugal	Panasqueira Borralha	Schist and grauwacke complex Micaschist and old granite	Tourmalination Greisenization and chloritization	290-280 m.y.	QI- W-(Sn) QII-Fe-Cu-Zn sulphides QIII-Pb-Bi-Ag- sulphosales QIV-chlorite- carbonates- adularia	Kelly & Rye (1979) Bussink (1984) Noronha (1974, 1984, 1990) Noronha et al (1992, 1995) Polya (1989)

Table I.- Comparison between Spanish Central System and Northern Portugal W-occurrences

analysis performed (at CREGU, Nancy) on a DILOR X-Y multichannel modular Raman spectrometer (Dhamelincourt *et al.*, 1979).

Bulk composition and molar volume were computed from the P-V-T-X properties of individual inclusions in the C-O-H-(N-S) system (Dubessy *et al.*, 1989, 1992; Thiery *et al.*, 1994a, 1994b; Thiery, 1996; Bakker, 1995; Bakker *et al.*, 1996). The P-T properties of aqueous-carbonic inclusions were modelled for the system $H_2O-NaCl-CO_2-CH_4$ using the V-X data and the Kerrick and Jacobs (1981) and Jacobs and Kerrick (1981) equations of state.

Classification of fluid inclusions: the microthermometric and Raman results

Prior to freezing and heating, all inclusions were studied and classified in order to outline the general characteristics of the fluid inclusion populations (primary, pseudosecondary or secondary) based on criteria proposed by Roedder (1984). Fluid inclusions have been studied as a function of the chronology of the vein infilling; new and previously published data have been considered in this study (Kelly and Rye, 1979; Bussink, 1984; Noronha, 1974, 1984, 1990; Quílez *et al.*, 1990; Noronha *et al.*, 1992; Quílez, 1994; Martin Romera, 1995; Vindel *et al.*, 1995, 1996; Noronha *et al.*, 1995; García, 1997).

Several fluid inclusion types were classified on the basis of microscopic, microthermometric and Raman data following the classification of Boiron *et al.*, (1992). Nomenclature of fluid inclusions is based on the type of global homogenization T_h (L-V to the vapour, noted V; L-V to the liquid, noted L), and the presence of C-H-O-(N-S) species detectable by Raman spectroscopy (subscript c when C-H-O-S species are dominant; c-w, when both water and C-H-O-S species are present; and w when C-H-O-(N-S) species are not detected by any methods). Microthermometric and Raman microprobe analyses carried out on selected fluid inclusions are given in Table II.

Based on microthermometric studies and Raman analysis three main types of fluids have been distinguished:

(i) *Hypersaline aqueous fluids ($H_2O-NaCl$)*: These fluids are represented by Lw-s inclusions (three-phase fluid inclusions) with one or more solid phases (dominantly halite and/or sylvite and unknown trapped minerals). They occur as primary fluid inclusions in newly formed quartz and as secondary fluid inclusion planes in the granite and close to the vein within the greisenised zone. Such type of fluid inclusions have not been observed either in the veins or away from the ore zones, and are specific to the Spanish Central System.

Total homogenisation temperatures (T_h) to the liquid phase ranges from 200–450 °C. Most of halite crystals melt just before or in the same range of temperature than T_h , yielding salinity estimation ranging from 29 to 53 wt % eq. NaCl.

These hypersaline aqueous fluids have been only observed in the Spanish Central System, and only in the wall-rock of the W-veins (muscovite-quartz assemblage) as fluid inclusions planes.

(ii) *"Metamorphic" aqueous-carbonic fluids ($H_2O-NaCl-CO_2-CH_4$)*: These fluids are represented by several types of aqueous-carbonic fluid inclusions and are observed in the different types of quartz. $H_2O-NaCl-CO_2-(CH_4)$ liquids in Lc-w inclusions showing two or three phases at room temperature, $CO_2(v)$, $CO_2(l)$ and $H_2O(l)$; these inclusions are observed as primary inclusions in quartz QI and are contemporaneous with the wolframite. They homogenise (global homogenisation) into the liquid phase (Lc-w) and more rarely into vapour (Vc-w).

Quartz QII shows only two-phase inclusions (Lw-c, Lw-m, Lw (c-m), homogenising into the liquid phase. They occur as isolated (primary) inclusions in clusters (pseudosecondary). It is assumed that the fluids (Lw-c, Lw-m and Lw (c-m)) are contemporaneous of the main sulphides deposition. A progressive enrichment in water and CH_4 content characterized the chemical evolution of fluids.

Mineralization	Fluid type	MICROTHERMOMETRY						BULK COMPOSITION				
		flw	TmCO ₂	TmI	TmCl	ThCO ₂	Th	Wt%NaCl	H ₂ O	CO ₂	CH ₄	N ₂
SPANISH CENTRAL SYSTEM	Lw-s	0.05/0.15					200/450*	29/53	71.0/47.0			
	Lc-w	0.2/0.7	-59/-56.7	-1.7/-4.8	6.0/10.0	19.0/26.0 V	300/385	0.6/5.1	71.7/89.0	9.3/25.5	nd/0.4	nd/1.7
	Vc-w	0.2/0.7	-60.0/-56.7		6.5/9.3		290/420	0.1/2.8	65.0/90.0	8.0/28.0	0.1/2.5	nd/3.5
	Lw-c	0.5/0.6		-7.0/-2.0	7.6/9.0		290/380	0.2/2.2	93.0/95.5	1.3/4.3	0.3/4.1	nd/1.1
	Lw-m	0.5/0.7		-6.0/-0.9	7.0/16.0		210/370	0.1/2.0	87.0/94.0	nd	4.9/12.6	nd
	Lw1	0.7/0.8		-5.8/-2.3			120/380	4.1/8.9	91.1/96.1			
BORRALHA	Lw2	0.8/0.9		-3.2/-1.5			90/150	2.6/5.3	94.7/97.4			
	Lc-w	0.3/0.5	-60.5/-58.2	-8.5/-7.0	5.0/8.0	10.0/20.0 V	260/320	1.3/6.3	83.2/97.0	2.9/13.2	nd/0.7	nd/1.9
	Vc-w	0.4/0.5	-60.5/-60.0	-8.0/-7.0	7.8/8.0	9.0/10.0 V	270/280	1.5/3.9	85.0/86.9	17.7/18.2	nd/0.7	nd/1.8
	Lw-(c-m)	0.7/0.8		-5.5/-1.7	5.0/6.4		192/274	0.3/4.5	93.7/97.0	2.9/5.3	nd/0.2	nd/0.4
	Lw1	0.8/0.9		-4.5/-2.2			204/243	4.0/7.3	92.7/96.0			
	Lw2	0.8/0.9		-2.7/-0.4			192/240	0.8/4.7	95.3/99.2			
PANASQUEIRA	Lc-w	0.7/0.8	-61.0/-59.0	-7.0/-2.0	6.5/10.8	-4.0/-1.2 V	226/350	0.1/1.1	93.1/94.4	4.1/4.9	0.1/0.2	0.6/1.1
	Vc-w	0.1/0.2	-62.0/-60.0				250/340					
	Lw-(c-m)	0.7/0.8		-5.7/-6.4	7.9/8.8		190/285	1.1/4.1	93.1/94.4	4.1/4.8	0.2/1.0	0.4/0.6
	Lw1	0.7/0.8		-2.0/-0.5			200/250	1.0/5.0	95.0/99.0			

* Melting of solid phase

Table II.- Raman data and bulk composition (in mole %) of selected fluid inclusions. Spanish Central System and Northern Portugal (Borralha, Panasqueira).

Homogenisation of the non-aqueous part (ThCO₂) occurs to the vapour at temperatures ranging from -4 to +29 °C. Melting temperatures of CO₂ (TmCO₂) are observed from -62 to -56.7 °C. TmCO₂ in all CO₂-bearing inclusions is lower than the melting temperature of pure CO₂ (-56.6 °C), indicating the presence of other volatile compounds rather than CO₂, such as CH₄ and N₂. This is confirmed by Raman microprobe analysis which shows that the composition of the volatile phase is, however, dominated by CO₂. N₂ has been detected by Raman probe in almost all the analysed inclusions, but N₂ is rather abundant at Panasqueira and Borralha with contents ranging from 12.5 to 19.9 mole % in the volatile phase (Fig. 2).

Global homogenisation temperatures occur to the vapour phase for Vc-w inclusions and range from 290 °C to 420 °C in SCS, 270 °C to 280 °C at Borralha and 250 °C to 340 °C at Panasqueira. Global homogenisation temperatures to the liquid phase, for Lc-w inclusions are in the range of 300 °C to 385 °C in SCS, 260 °C to 320 °C at Borralha and 226 °C to 350 °C at Panasqueira (Table II).

(iii) *Aqueous fluids (H₂O-NaCl) liquid*: Aqueous fluid inclusions are abundant. The classification of aqueous inclusions have been made according to two parameters: the degree of filling (flw) and the melting temperature of ice (TmI). No volatile species (CO₂, CH₄) were identified either by microthermometry or Raman spectroscopy. Two main types of inclusions (Lw1, Lw2) have been distinguished:

a) Lw1 are two-phase aqueous inclusions with flw ranging from 0.7 to 0.8 and Tmice in between -5.8 and -0.5 °C and Th between 120 and 380 °C;

b) Lw2 are two-phase aqueous inclusions with flw range between 0.8 and 0.9 and Tmice between -3.2 and -0.4 °C and Th between 90 and 240 °C.

Lw1 type has been observed in QI and QII as secondary inclusions; QIII shows primary two-phase inclusions (Lw2) homogenising into the liquid phase. The latter aqueous fluid inclusions (Lw2) are only found as secondary FIP in QI and QII. A third type of

two-phase inclusions, very scarce, small (<5-10 μm), and usually metastable, with high flw (> 0.9) can be present.

Chronological relationships between fluid inclusion types

The relationships between Lc-w and Vc-w inclusions in QI were interpreted as fluids related with the beginning of tungsten deposition. The microthermometric and Raman data showed that some immiscibility took place between the two fluids. Lw-c, Lw-m and Lw-(c-m) are posterior to the precedent ones and are related to the end of tungsten deposition and mark the beginning of sulphide stage.

The spatial relationships between CH₄ bearing inclusions and the main sulphides indicates that the sulphide stage is not disconnected from the whole evolution of the first hydrothermal stage "oxide silicate stage" in the Spanish Central System examples (Fig. 2).

Lw1 inclusions represent an overprint by later, dominantly aqueous, fluids post-"oxide silicate stage" and "main sulphide stage". The late aqueous fluids (Lw2) are related to microfissure opening but not related to the main sulphide stage.

Bulk chemical evolution and P-T estimation

The bulk composition of some selected aqueous-carbonic fluid are present in Table II. A compositional trend of increasing XH₂O fraction at decreasing volatile content from Vc-w to Lw-c and Lw-m inclusions can be observed. This compositional evolution is also marked by a decrease in the density of the volatile phase (Fig. 3). The evolution is characterised by low ZCH₄ + ZN₂ content (1 to 25% ZCH₄) in the early stage to an intermediate stage with high CH₄ content and low density volatile phase in the Lw-m fluids.

The P-V-T-X properties of C-H-N-O inclusions (Lc-w and Vc-w) were modelled in the H₂O-CO₂-CH₄ system using the equations of state of Kerrick and Jacobs (1981) and Jacobs and Kerrick (1981) and the data given in Table II. The isochores relative to aqueous

(Lw) were modelled in the H_2O - NaCl system fluids (Zhang and Frantz, 1987; Bodnar, 1993).

The P-T path (Fig.4) is a schematic representation of the ore deposition evolution using previous calculated isochores (Vindel *et al.*, 1995; Noronha, 1984; Kelly and Rye (1979). They are characterised by a nearly isobaric evolution corresponding to the period of tungsten deposition "oxide silicate stage" related to aqueous-carbonic fluids at pressures ranging from 150 to 50 MPa and temperatures from 300 to 520 °C (Vindel *et al.*, 1995; Boiron *et al.*, 1996). The highest P and T values (130 MPa and 520 °C) are found in Spanish examples and the lowest pressures in Portuguese deposits, namely at Panasqueira (50 Mpa) (Kelly and Rye, 1979; Noronha, 1984).

The spatial relationship between more diluted fluids (CH_4 bearing), and the "main sulphides stage" indicates a crystallisation of these minerals at 100 to 30 MPa and 300 to 370 °C. This also indicates that the sulphide stage is not disconnected from the evolution of this hydrothermal cycle that began with CO_2 rich fluids.

A brittle microfracturing stage is then well developed allowing low temperature aqueous fluids to circulate in relatively shallow crustal levels. The late aqueous fluids could be related to microfissure opening but are no related to the main depositional stages (Noronha *et al.*, 1995; Boiron *et al.*, 1996).

Discussion

A genetic relationships between the Iberian hydrothermal W-Sn mineralization and their surrounding granites are generally considered. The results of the present study show that the Iberian Hercynian granites may be regarded as playing a different role in ore forming processes than previously thought. All the fluid types are essentially sodium and chlorite-rich, specially during the "oxide silicate stage" (Noronha, 1984; Polya, 1989; Noronha *et al.*, 1992). Stuart *et al.* (1996) studying crystal of cassiterite, wolframite, arsenopyrite and quartz from de "main sulphide stage" from Panasqueira found δD values varying from -40 to -130 what suggest a mixture of different types of fluids.

W-ore fluids may have from two origins: i) magmatic processes or ii) processes involving the surrounding rocks. The Lc-w and Vc-w can be better explained as resulting from the water-rock interaction within the metamorphic surrounding rocks ("metamorphic fluids") because CO_2 -rich fluids cannot be evolved from differentiated granitic magmas as the very low CO_2 solubility in such magmas (Shilobreeva and Kadik, 1987). The CO_2/CH_4 ratio point to reactions between H_2O and graphite at temperatures approximately around 400 °C (Dubessy, 1984; Dubessy *et al.*, 1989).

Therefore, the main role of the granites was to supply a heat source, because no typical magmatic

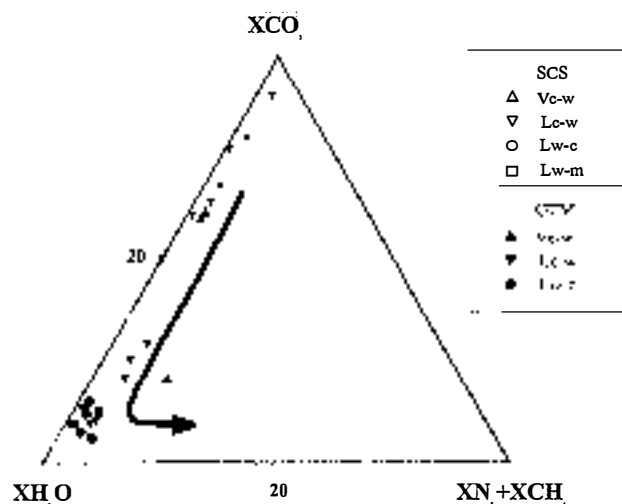


Figure 2.- XH_2O - XCO_2 - XCH_4 + XN_2 ternary plot of type Vc-w, Lc-w, Lw-c and Lw-m inclusions. SCS: Spanish Central System. GTM: Galicia-Trás-os-Montes.

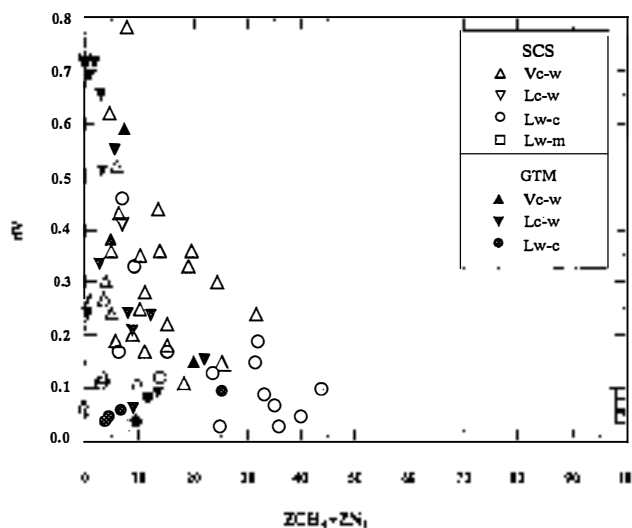


Figure 3.- Binary volatile density (dv)- ZCH_4 of type Vc-w, Lc-w, Lw-c and Lw-m inclusions. SCS: Spanish Central System. GTM: Galicia-Trás-os-Montes.

signature is found except in the earliest stages associated with the granites like in SCS (muscovite stage). The first stage of tungsten deposition is always characterised by the presence of aqueous-carbonic fluids at relatively low pressures ranging from 150 to 50 MPa; however the pressure is lower on Portuguese deposits (<80 MPa) than the Spanish ones (100 to 150 Mpa) (Kelly and Rye, 1979; Noronha, 1984; Vindel *et al.*, 1995; Boiron *et al.*, 1996). This can be justified by the location of SCS mineralisations at a deeper structural level, as they occur on a Precambrian gneissic basement, contrarily to the Portuguese mineralisations that occur on metasediments with medium to low grade regional metamorphism affected by posterior contact metamorphism (Panasqueira is a good example of shallower mineralisations). The thermal metamorphism

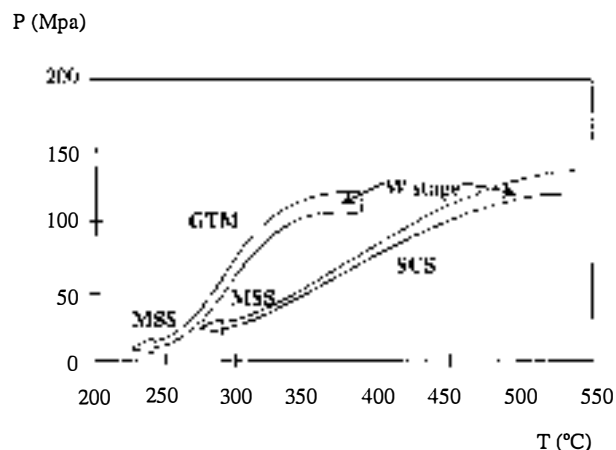


Figure 4.- P-T reconstruction of conditions prevailing for the tungsten occurrences of northern Portugal and Spanish Central System. SCS: Spanish Central System. GTM: Galicia-Trás-os-Montes. W stage: wolframite stage. MSS: main sulphide stage.

can also justify higher N_2 content on the early stages of Portuguese examples.

A progressive enrichment in H_2O and CH_4 content and decrease in the density of the volatile phase is demonstrated. CH_4 rich fluids are interpreted as the result of progressive dilution of early fluids yielding to fluid compositions characterised by rather low volatile contents. The volatile phase is dominated by methane due to the sluggish kinetics of fluid-graphite reactions below 400 °C. This indicates that the sulphide stage is not disconnected from the first hydrothermal cycle in the SCS (Vindel *et al.*, 1995).

The general evolution implies cooling and dilution of a volatile-rich fluid by cooler fluids of aqueous composition. The scattering of total homogenisation temperatures, together with the variable degree of filling and the consequent variation on fluids density, may result from fluid pressure fluctuations below lithostatic pressure in relation with deformation.

Conclusions

W-ore fluids in Northern Portugal and Central Spain are in all cases characterised by the presence of a volatile (CO_2 - CH_4 - N_2) component, resulting from water-rock interactions within the surrounding metamorphic host rocks. These fluids belong to the C-H-O-N system and are mostly dominated by CO_2 - H_2O waters circulating through metamorphic rocks where they acquired most of their chemical features. A progressive enrichment in water and CH_4 content as well as a decrease in the density of the volatile phase occurs correlatively to a temperature decrease. In Portugal, the amount of CH_4 is much less than those found in Spain, probably because the late sulphide stages characterized by low temperatures (< 350 °C) is least developed than in Spain.

In all deposits, there is evidence of series of fracturing events allowing to late aqueous fluids circulate at relatively shallow crustal levels and under at low P-T conditions. Data show that the Hercynian

granites may be regarded as playing a different role on ore forming processes than already thought, as no typical magmatic signature is found except in the earliest stages responsible for the greisen formation. The main role of the granites appears to be a heat supply which favoured the circulation of non magmatic fluids in the metamorphic environment.

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References

- Bakker, R.J. (1995): The application of a computerised and optimised clathrate stability model to fluid inclusion studies. *Bol. Soc. Esp. Min. XIII ECROFI Conference*, 18-1: 15-17.
- Bakker, R.J., Dubessy, J., Cathelineau, M. (1996): Improvements in the clathrate modelling: I. The H_2O - CO_2 system with various salts. *Geochim. Cosmochim. Acta*, 60: 1657-1681.
- Bodnar, R.J. (1993): Revised equation and table for determining the freezing point depression of H_2O -NaCl solutions. *Geochim. Cosmochim. Acta*, 57: 683-684.
- Boiron M.C., Essarraj, S., Sellier, E., Cathelineau, M., Lespinasse M. & Poty B. (1992) Identification of fluid inclusions in relation with their host microstructural domains in quartz by cathodoluminescence. *Geochim. Cosmochim. Acta*, 56: 175-185.
- Boiron, M.C., Cathelineau, M., Noronha, F., Banks, D., Vindel, E. & Lopez, J.A. (1996): From retrograde Hercynian metamorphism to granite related to geothermal fields: a fluid chemistry and P-T-Depth reconstruction based on fluid inclusions. *VI PACROFI, Madison, Brown and Hagemann Eds.*, 18-20.
- Bussink, R.W. (1984): Geochemistry of the Panasqueira tungsten-tin deposit, Portugal. *Geologica Ultraiectiona*, 33, 170 p.
- Caballero, J. M., Casquet, C., Galindo, C., Gonzalez-Casado, J. M., Snelling, N. & Tornos, F. (1992): Dating of hydrothermal events in the Sierra de Guadarrama, Iberian Hercynian Belt, Spain. *Geogaceta*, 11: 18-22.
- Dhamelincourt, P., Beny, J., Dubessy, J., & Poty, B. (1979): Analyse d'inclusions fluides à la microsonde MOLE à effet Raman. *Bull. Soc. Franç. Minér.*, 102: 600-610.
- Dubessy, J. (1984): Simulation des équilibres chimiques dans le système C-O-H: conséquences méthodologiques pour les inclusions fluides. *Bull. Minéral.*, 107: 155-168.
- Dubessy, J., Poty, B., Ramboz, C. (1989): Advances in the C-O-H-N-S fluid geochemistry based on micro-Raman spectroscopic analysis of fluid inclusions. *Eur. J. Mineral.*, 1: 517-534.
- Dubessy, J., Thiery, R., Canals, M. (1992): Modelling of phase equilibria involving mixed gas clathrates: Application to the determination of molar volume of the vapour phase and salinity of the aqueous solution in fluid inclusions. *Eur. J. Mineral.*, 4: 873-884.
- Ferreira, N., Iglésias, M., Noronha, F., Pereira, E., Ribeiro, A. & Ribeiro, M.L., (1987): Granitoides da Zona Centro Ibérica e seu enquadramento geodinâmico. En: *Geologia de los granitoides y rocas asociadas del Macizo Hespérico*. Libro

- homenaje a L.C.García de Figuerola. Editorial Rueda, Madrid, 37-51.
- García, E. (1997): *Análisis de la circulación hidrotermal en granitos mineralizados con W-Sn (Sierra de Guadarrama)*. Tesis Doctoral, Universidad Complutense, Madrid. 259 p. (inérita).
- Jacobs, G.K. & Kerrick, D.M. (1981): Methane: an equation of state with application to the ternary system H_2O - CO_2 - CH_4 . *Geochim. Cosmochim. Acta*, 45: 607-614.
- Kelly, W.C. & Rye, R.O. (1979): Geologic, fluid inclusions and stable isotopic studies of tin-tungsten deposits of Panasqueira, Portugal. *Econ. Geol.*, 74: 1721-1822.
- Kerrick, D.M. & Jacobs, G.K. (1981): A modified Redlich-Kwong equation for H_2O , CO_2 and H_2O - CO_2 mixtures at elevated pressures and temperatures. *Amer. Jour. Sci.*, 281: 735-767.
- Mangas, J. (1987): Fluid inclusion study in different types of tin deposits associated with the Hercynian granites of western Spain. *Chem. Geol.*, 61: 193-208.
- Martin Romera, C. (1995): *Estudio de las pegmatitas asociadas a la mineralización de W de Cabeza Lijar (Sistema Central Español): relaciones entre paleofluidos y deformaciones*. Tesis de Licenciatura, Univ. Complutense, Madrid. 112 p. (inérita).
- Noronha, F. (1974): Étude des inclusions fluides dans les quartz des filons du gisement de tungstène de Borralha (Nord du Portugal). *Publicações do Museu e Laboratório Mineralógico e Geológico da Faculdade de Ciencias do Porto*. 4ª Sér., 45.
- Noronha, F. (1984): Caractéristiques physico-chimiques des fluides associés a la genèse du gisement de tungstène de Borralha - Nord du Portugal. *Bull. Minéral.*, 107: 273-284.
- Noronha, F. (1990): Dedução de condições físico-químicas de formação de jazigos hidrotermais através do estudo de inclusões fluidas. O exemplo de alguns jazigos portugueses. *Boletim da Academia Galega de Ciências*, Santiago de Compostela, 9: 86-126.
- Noronha, F., Doria, A., Dubessy, J. & Charoy, B. (1992): Characterisation and timing of the different types of fluids present in the barren and ore-veins of the W-Sn deposit of Panasqueira, Central Portugal. *Mineral. Deposita*, 27: 72-79.
- Noronha, F., Doria, A., Nogueira, P., Boiron, M. C. & Cathelineau, M. (1995): A comparative study of the fluid evolution in late-hercynian W (Sn-Cu) and Au (As) quartz veins in Northern Portugal. Metallogenic implications. En: IV Congresso Nacional de Geologia. Resumos alargados. (F. Sodrê Borges & M. M. Marques, Coords.) *Mem. Mus. Labor. Miner. Geol. Fac. Ciências. Univ. Porto*, 4: 587-592.
- Pinto, M.S., Casquet, C., Ibarrola, E., Corretgé, L.G. & Ferreira, M.P. (1987): Síntese geocronológica dos granitoides do Maciço Hespérico. En: *Geologia de los granitoides y rocas asociadas del Macizo Hespérico*. Libro homenaje a L.C.García de Figuerola. Editorial Rueda. Madrid, 69-86.
- Polya, D. (1989): Chemistry of the main-stage ore-forming fluids of the Panasqueira W-Cu(Ag)-Sn Deposit, Portugal: Implications for models of ore genesis. *Econ. Geol.*, 84: 1134-1152.
- Potter, R.W. (1977): Pressure corrections for fluid inclusion homogenisation temperatures based on the volumetric properties of the system $NaCl$ - H_2O . *J. Res. U.S. Geol. Surv.*, 6: 245-257.
- Potter, R.W., Clynne, M.A. & Brown, D.L. (1978): Freezing point depression of aqueous sodium chloride solutions. *Economic Geology*, 73: 284-285.
- Poty, B., Leroy, J. & Jachimowicz, L. (1976): A new device for measuring the temperatures under the microscope: the Chaixmeca microthermometry apparatus. *Bull. Soc. franc. Minéral. Cristallogr.*, 99: 182-186.
- Quílez, E., Vindel, E. & Sierra, J. (1990): A fluid inclusion study and genetic model of wolframite-bearing quartz veins, Garganta de los Montes, Spanish Central System. *Min. Magazine*, 54: 267-278.
- Quílez, E. (1994): *Mineralizaciones filonianas de wolframio de la Sierra de Guadarrama: modelo y caracterización del proceso hidrotermal*. Ph D. Thesis, Univ. Complutense, Madrid, 277p.
- Roedder, E. (1972): Composition of fluid inclusions. *U.S. Surv. Prof. Paper*, 440: 164 p.
- Roedder, E. (1984): Fluid inclusions. *Mineral. Soc. America Reviews in Mineralogy*, 12: 644 p.
- Shepherd, T.J. (1981): Temperature programmable heating freezing stage for microthermometric analysis of fluid inclusions. *Econ. Geology*, 76: 1244-1247.
- Shilobreeva, S.N. & Kadik, A.A. (1987): Carbon and its volatile compounds in silicate melts and crystals: Experimental data. *Proc. First Indo-Soviet workshop on Exp. Min. Petrol.*, New Deli, 39-41.
- Stuart, F.; Boyce, A., Foxford, A.; Polya, D. & Fallick, A. (1996): Constraints on the origin of low δD hydrothermal fluid inclusions from halogen and Ar isotopes: evidence from Panasqueira W-Sn mine, Portugal. *Pacofi VII.*, 129-131.
- Thadeu, D. (1977): Hercynian paragenetic units of the Portuguese part of the Hesperic Massif. *Bol. Soc. Geol. Portg.*, 20: 247-276.
- Thiery, R. (1996): *Les systèmes eau-gaz-sels. Modelisation des équilibres de phases et application aux fluides géologiques*. Ph D. Thesis, INPL Nancy, 227p.
- Thiery, R., Van den Kerkhof, A.M. & Dubessy, J. (1994a): V-X properties of CO_2 - CH_4 and CO_2 - N_2 fluid inclusions: modelling for $T < 31^\circ C$ and $P < 400$ bars. *Eur. J. Mineral.*, 6: 753-771.
- Thiery, R., Vidal, J. & Dubessy, J. (1994b): Phase equilibria modelling applied to fluid inclusions: liquid-vapour equilibria and calculation of the molar volume in the CO_2 - CH_4 - N_2 system. *Geochim. Cosmochim. Acta*, 58: 1073-1082.
- Villaseca, C., Barbero, L. & Andonaegui, P. (1993): Diversity of peraluminous granites types in Hercynian Central zone of Spain. *Terra Abstract*, 5: 433-434.
- Vindel, E. (1980): *Estudio mineralógico y metalogénico de las mineralizaciones de la Sierra de Guadarrama*. Ph D. Thesis, Univ. Complutense, Madrid, 249 p. (inérita).
- Vindel, E., López, J.A., Boiron, M. C., Cathelineau, M. & Prieto, A. C. (1995): P-V-T-X- fO_2 evolution from wolframite to sulphide depositional stages in intragranitic W-veins. An example from the Spanish Central System. *Eur. J. Mineral.*, 7: 655-673.
- Vindel, E., López, J. A., García, E., Boiron, M. C. & Cathelineau, M. (1996): Estudio de inclusiones fluidas en granitos microfisurados. Mineralizaciones de W-Sn del Sistema Central Español. *Geogaceta*, 20(7): 1558-1560.
- Zhang, Y.G. & Frantz, J.D. (1987): Determination of the homogenisation temperature and densities of supercritical fluids in the system $NaCl$ - KCl - $CaCl_2$ - H_2O using synthetic fluid inclusions. *Chemical. Geol.*, 64: 335-350.

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